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AEROJET ORDNANCE AND MANUFACTURING COMPANY
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DETERMINATION OF DECONTAMINATION CRITERIA

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DIMP AND DCPD (U)

Report No. 1953-01-(04)MP

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13. ABSTRACT *(Maximum 200 words)*
THIS IS A PROGRESS REPORT ON AEROJET'S STUDIES OF EXPERIMENTS CURRENTLY UNDERWAY (E.G., PLANT GROWTH AND DIMP AND DCPD LYSIMETER TESTS). TESTS ARE IN PROGRESS TO DETERMINE THE STABILITY OF DIMP AND DCPD IN INTIMATE CONTACT WITH MOISTENED TOP SOIL. THE ANALYTICAL METHOD PROPOSED FOR DCPD WILL REQUIRE SOME MODIFICATION. THREE OF THE FIVE SOILS TO BE USED IN THE LYSIMETER EXPERIMENTS HAVE BEEN OBTAINED, PROCESSED AND LOADED INTO SIX LYSIMETERS. DISTILLED WATER HAS BEEN PASSED THROUGH ALL OF THEM. TEN PLANTS OF ONE PLANT EACH OF THE PLANTS ENUMERATED IN LAST MONTHS' REPORT HAVE BEEN STARTED IN WATER CULTURE BATHS. PLANT TEST TUBS WERE INOCULATED WITH CONTAMINANTS, CONDITIONS AND PHYTOTOXIC SYMPTOMS WERE NOTED.

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Progress on items proposed for action during October 1975, is discussed in the following paragraphs.

SOIL/AGENT COMPATABILITY TESTS

Tests are in progress to determine the stability of DIMP (diisopropyl methylphosphonate) and DCPD (dicyclopentadiene) in intimate contact with moistened Chino top soil. This soil is from the same location as that designated as "Chino soil" in the lysimeter experiments described elsewhere in this report.

The analytical method proposed for DCPD was described in 1953-01(03)MP. This will require some modification due to the volatility of the DCPD resulting in significant loss of agent on concentration. This problem is being investigated.

The analytical method for DIMP consists of extracting the appropriate sample with methanol by intimately mixing, followed by centrifugation to remove the insoluble portion of the sample and gas-liquid chromatography of the resulting supernatant liquid.

Approximately one microliter samples are injected into a Varian gas-liquid chromatograph fitted with an alkaline flame ionization detector (AFID) specifically tuned to detect phosphorus containing compounds. The column used consists of a four foot by 1/8 inch stainless steel Gas Chrom Q column containing a 10% w/w QF-1 liquid phase. The sample is chromatographed at 115°C and 10 PSI (NOM.) and the peak areas used for quantitation. Standard solutions of DIMP in the same concentration ranges as the samples are chromatographed for comparison. Figures 1 and 2 show typical DIMP chromatograms using this system. The samples presented to the chromatograph in this case were 0.1 ppm DIMP in methanol (1×10^{-7} g/cc) and 1 ppm DIMP in methanol (1×10^{-6} g/cc).

The shaded areas on the chromatograms are the peaks due to the presence of DIMP. Control samples show no peak at this retention time. A series of standards run in this fashion resulted in the standard curve shown in Figure 3. The nature of the AFID detector is such that minor fluctuations in fuel/air flow ratios can cause variations in detector output and therefore standard solutions must be run in conjunction with each series of samples for the greatest accuracy.

The soil test itself consists of a series of 500 ml. erlenmeyer flasks each containing 150 grams of virgin top soil from the Chino area which has been wet with 37.5 ml. distilled water. Filtered air, moistened by bubbling through distilled water, is slowly passed through the flasks. After passing through the various flasks the air is led into a series of cold traps containing methanol which are housed in a laboratory refrigerator. The DIMP and DCPD are each added to a separate series of flasks in concentrations of 0.1, 1, 10, 100 and 1000 parts per million based on dry soil weight. If vaporization or decomposition of the agent occurs (i.e., bacterial, oxidative, etc.) an analysis of the soil will demonstrate its absence. If vaporization is significant, the methanol traps should contain significant quantities of agent. Radioactive tracing of CO_2 produced by microbial action is not being conducted.

Figure 4 shows the experimental setup in operation.

Early data from these tests is shown in Table I.

Table I

Recovery of DIMP from Top Soil Samples

DIMP Concentration (ppm) Calculated	% of DIMP Concentration Found: In Soil After 15 Days	In Soil After 21 Days	In MeoH Trap 22 Days
0.1	125	137	---
1.0	63	69	---
10.0	65	54	0.83
100.0	54	64	0.38
1000.0	37	29	0.45

Plotting this data gives the curves in Figure 5. Although further data will be needed for confirmation it appears that an initial loss occurs followed by a plateauing. This type of behavior would be compatible with that found in a previous program where DIMP was found in weathered, outdoor soil after at least six years exposure to the elements. The behavior of the 0.1 ppm sample can not be explained as yet but is obviously atypical and an explanation is being sought in the analytical handling procedures.

A small amount of DIMP was found ($< 1\%$) in the methanol traps. Further work is required to determine whether this small value is due to limited vaporization from the soil or is due to revolatilization from the traps.

Additional samples of the DIMP and DCPD inoculated soils await analysis. These analyses will increase the stability time-base for the two compounds.

Additional efforts to develop concentrating methods for the DCPD extracts are required due to the relative volatility of the DCPD and the lack of sensitive specific detectors for the hydrocarbon such as the one used with the phosphonate.

PREPARATION OF FULL SCALE LYSIMETER TESTS

Three of the five soils to be used in the lysimeter experiments have been obtained, processed and loaded into six lysimeters. Distilled water has been passed through all of them. A fourth type has been located and permission obtained to procure the soil from the California State University at Fullerton Arboretum. The relationship of the sample site to the University property is shown in Figure 6. The three which are in place are a sandy clay loam from the AOMC property in Chino Hills, the classification of which is shown in Figure 7, a silty clay from Brawley, California and a sandy loam from Ventura, California. The Brawley sample was obtained from Dr. Burl Meek at the Imperial Valley Conservation Research Center. This area is shown in Figure 8, the actual profile of the sample hole can be seen in Figure 9. The Ventura sample was obtained from E. L. Barnhardt at the Limoneira Company Ranch. All of these soils are currently undergoing analysis by Dr. J. P. Martin.

The general geographical location of the first four samples is shown in Figure 10.

RANGE-FINDING PLANT GROWTH EXPERIMENTS

Ten sets of one plant each of the plants enumerated in last month's report (1953-01(03)MP) have been started in water culture baths. The baths are set up as shown in Figure 11. The contents of two tubs comprise one complete concentration group. The two tubs are set up as follows.

Table II

Range Finding Plant Arrangement		
Plant Holder	Tub 1	Tub 2
A	Bean	Tomato
B	Juniper	Wheat
C	Corn	Carrot
D	Empty	Empty
E	Empty	Empty
F	Empty	Empty
G	Rose	Sugar Beet
H	Empty	Empty
I	Radish	Fescue

The rose and juniper plants were transplanted from their original nursery containers into the hydroponic system with no visible evidence of transplant shock. The remaining plants were seeded in the laboratory germination beds and transplanted into the hydroponic system at various times depending on their size, e.g. corn and beans being much faster growers were transplanted earlier than carrots or sugar beets. After equilibrating with the system groups of ten healthy plants each were selected for the experiment and those other plants showing evidence of transplant shock or other non-optimum growth characteristics were discarded.

On October 16, the test tubs so designated were inoculated with DIMP resulting in concentrations of DIMP in the nutrient solution of 0, 1, 10, 100 and 1000 parts per million. On October 21, a similar group of tubs was inoculated with DCPD in the same concentrations. After ten days the DIMP containing

tubs were replenished with DIMP bringing them back up to their original concentration. At this time also additional Hoagland No. 2 nutrient mix was added to replenish that consumed by the plants.

Colored photographs were taken at intervals to document the gross symptoms of phytotoxicity. In the first four days after inoculation the tomato, sugar beet, bean, and radish at the 1000 (ppm) part per million DIMP level showed severe leaf damage. The rose under the same conditions showed minimal damage to the leaves. The other plants, i.e., corn, juniper, wheat, fescue and carrot appear unaffected.

After 14 days all of the 1000 ppm DIMP plants were apparently dead with the exception of the juniper plant which again appeared to be unaffected. In the 100 ppm DIMP system the following symptoms appeared.

Bean	- Slightly stunted, leaf curl.
Radish	- Slight leaf burn.
Rose	- Very slight leaf burn
Tomato	- Leaf burn.
Sugar Beet	- Leaf burn.
Carrot	- Leaf(tip) burn.

Other notable symptoms in the DIMP system were:

a. Larger than control plants in the case of the 10 ppm corn and beans, and the 1 and 10 ppm roses and the 1, 10 and 100 ppm tomato. This phenomenon of increased growth with the addition of various contaminants (e.g. insecticides) has been noted elsewhere.

At 15 days after inoculation, assay of all the 1000 ppm DIMP plants was begun. Also samples of tomato leaves from the other concentrations were analyzed. Table III reports the data from these analyses as well as data from the 1000 ppm bean plant. Figure 12 is a composite gas liquid chromatogram of methanol extracts analyzed for DIMP. The pertinent characteristics of the chromatograms are retention time and area under the curve.

It will be noted that the tomato plants at all levels of contamination demonstrated bio-accumulation of DIMP, the concentration factor varying from approximately 5 x in the leaves of the living 10 ppm sample to 15 x in the leaves of the apparently dead 1000 ppm sample. The apparently dead bean sample also showed a large bioaccumulation factor of 8x in the leaves. The bean root was the only sample containing less DIMP than the nutrient solution.

It has been noted in previous work at AOMC that dead and/or dried samples often contained higher concentrations of chemical contaminants than did their healthy counterparts. In large part this phenomenon is a mathematical artifact due to the loss of water weight on drying. However, the living plants did show an accumulation factor of 5 to 10x. These are relatively young plants and it has also been noted in other work at AOMC that young plants do absorb contaminants more rapidly than older ones. Analyses of the other plant species are underway and it is expected that a relationship between bio-accumulation and age will be developed for all of the plants tested.

Additional data on the DCPD uptake will be generated in the near future. Gross phytotoxicity observations of the plants grown in the DCPD contaminated nutrient showed the following symptoms for the 1000 ppm DCPD after ten days:

Corn	- Severe leaf burn and stunting
Rose	- Stunting

Table III

DIMP Content of Selected Plant Samples

Contamination Level (ppm DIMP)	Plant Type	Time From Inoculation (days)	Leaves (ppm)	Sample Wt. (g)	Roots (ppm)	Sample Wt. (g)	Stems (ppm)	Sample Wt. (g)
1.0	Tomato	13	10.4	0.4585	-	-	-	-
10	Tomato	13	50.9	0.7465	-	-	-	-
10	Tomato	13	59.0	0.7465	-	-	-	-
100	Tomato	12	501	0.9372	-	-	-	-
1000	Tomato	15	15,123	0.3141*	4,674	0.3070*	3,040	1.3750*
1000	Bean	15	8,000	0.6437*	729	1.8652*	2,018	1.4565*

* These weights constitute the entire plant.

Radish	- Leaf burn and stunting
Sugar Beet	- Leaf burn
Carrot	- Stunting and leaf chlorosis
Tomato	- Stunting

Colored photographs have been taken to document these conditions. The remainder of the DCPD treated plants have not evidenced gross toxicity symptoms as yet except for a generally poorer appearance than the control plants. These plant uptake (range-finding) experiments are continuing.

Visit by Consulting Scientist

On October 29, a visit was made to the AOMC Chino laboratory by Dr. Alva A. App of Boyce Thompson Institute. Experimental procedures were reviewed and the newest program protocol was discussed.

PROPOSED ACTIVITY DURING NOVEMBER 1975

During the coming month the following activities will be pursued:

- Continuation of the range finding plant growth experiments.
- Procurement and preparation of soils for the full scale lysimeter studies.
- Continue laboratory scale soil/additive experiments.
- Work up new test plans based on most recent protocol.

Operator POD	Date 10-10-75
Column	Detector AFID
Length 4'	Voltage
Dia. 1/8"	Sensit. 1x10^{-12}
Liquid Phase QF-1	Flow Rates, ml/min
Wt. % 10	Hydrogen AAR Air AAR
Support GAS-Chrom Q	Scavenge
Mesh 60-80	Split
Carrier Gas He	Temperature, °C
Rotameter	Det. 220 Inj. 200
Inlet Press. 12.5 psig	Column Initial 115
Rate ml/min	Final 115
CHART SPEED 1"=5 min.	Rate
SAMPLE DIMP	Solvent MeOH
Size 1.72	Concn. 0.1 ppm

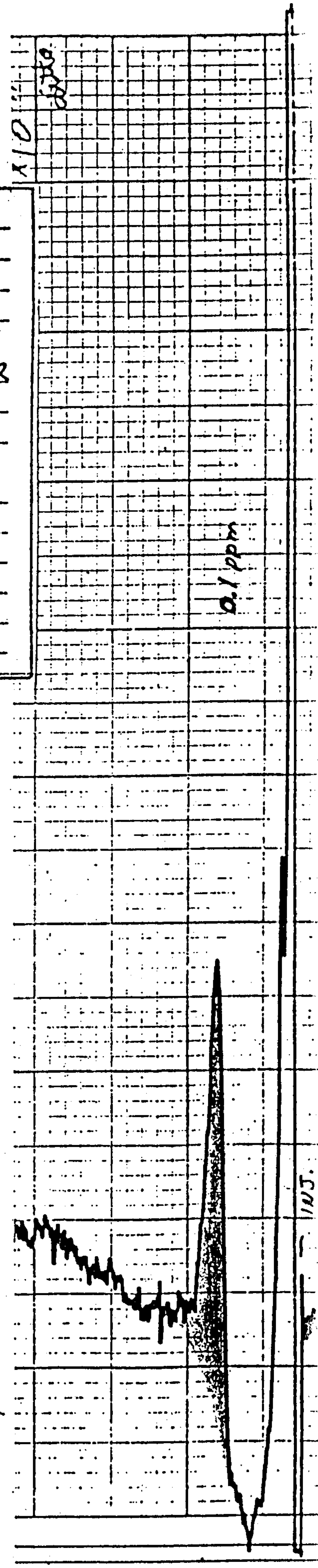


Figure 1. Chromatogram of 0.1 ppm DIMP in Methanol.

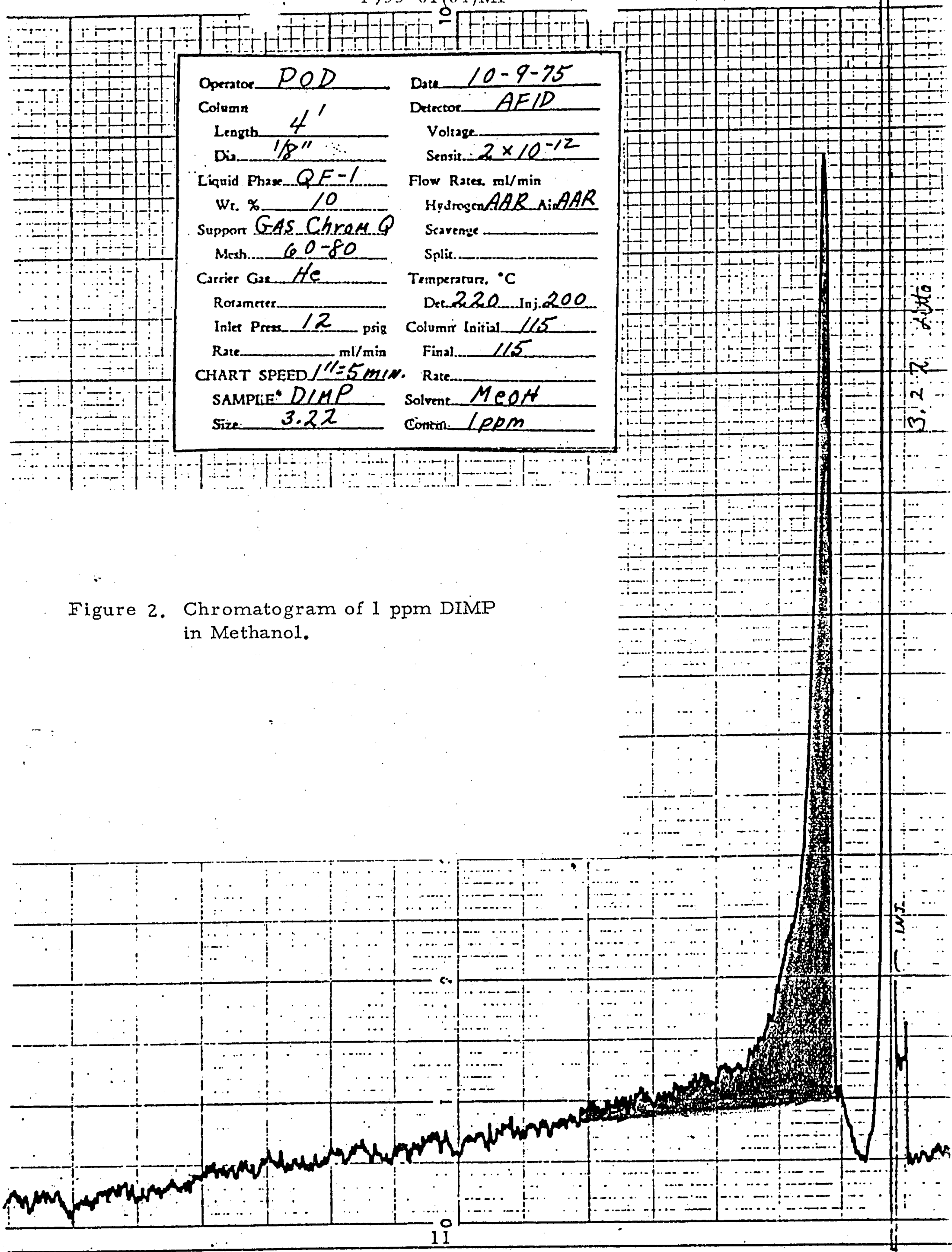


Figure 2. Chromatogram of 1 ppm DIMP in Methanol.

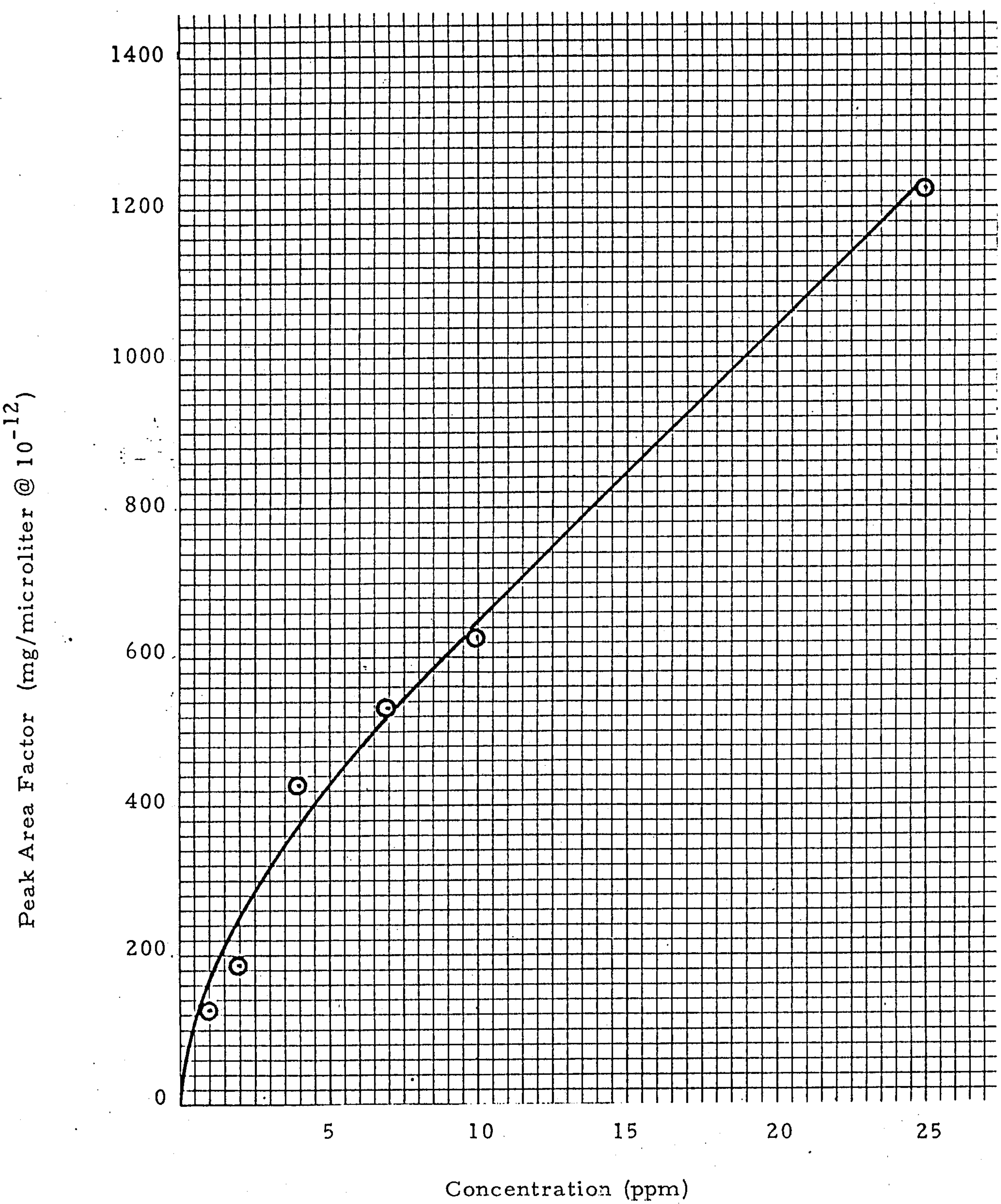


Figure 3. Standard Curve. Diisopropyl Methylphosphonate in Methanol, AFID Detector 10-20-75.

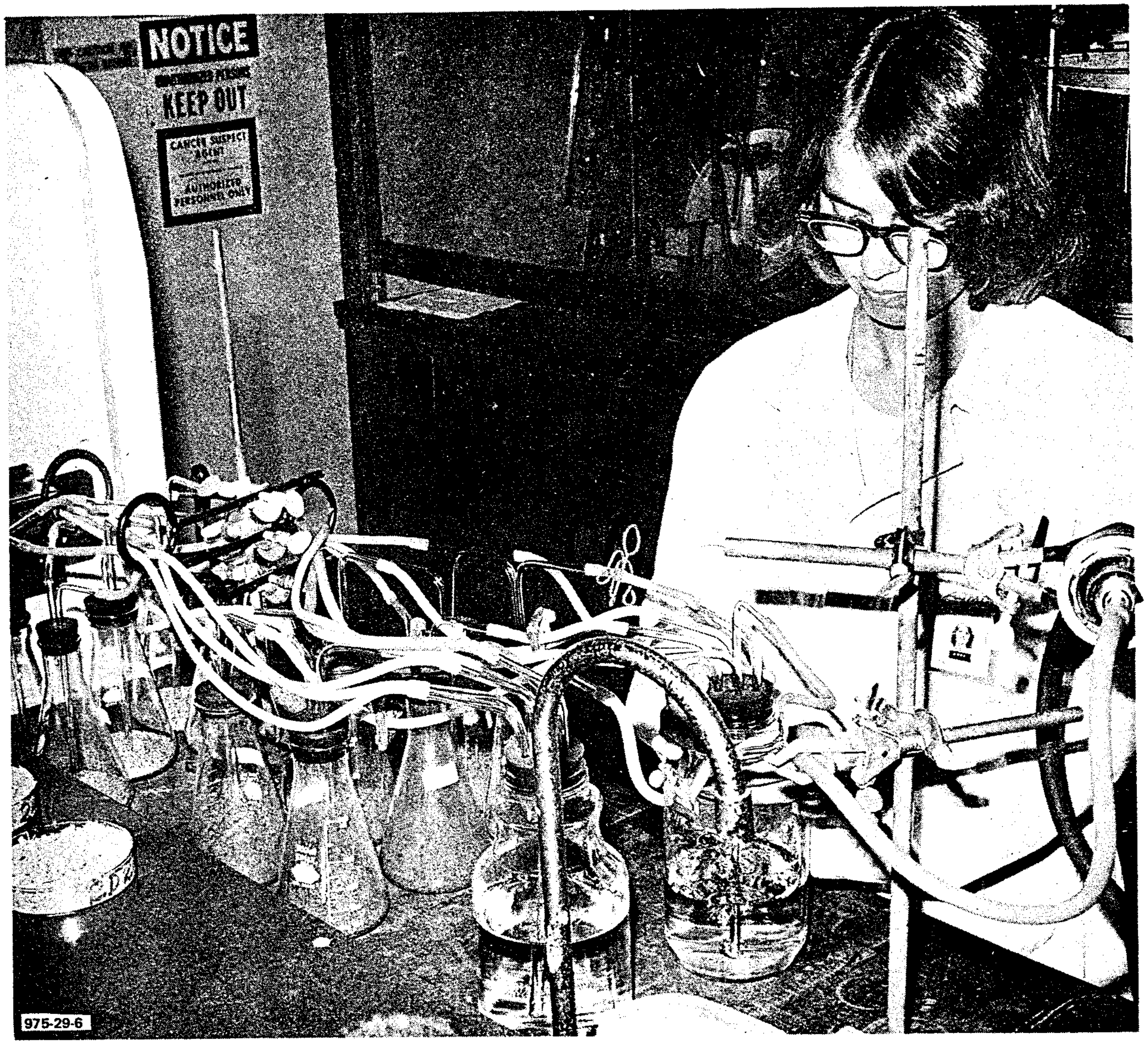


Figure 4. Experimental Setup for Soil/Agent Compatibility Tests.

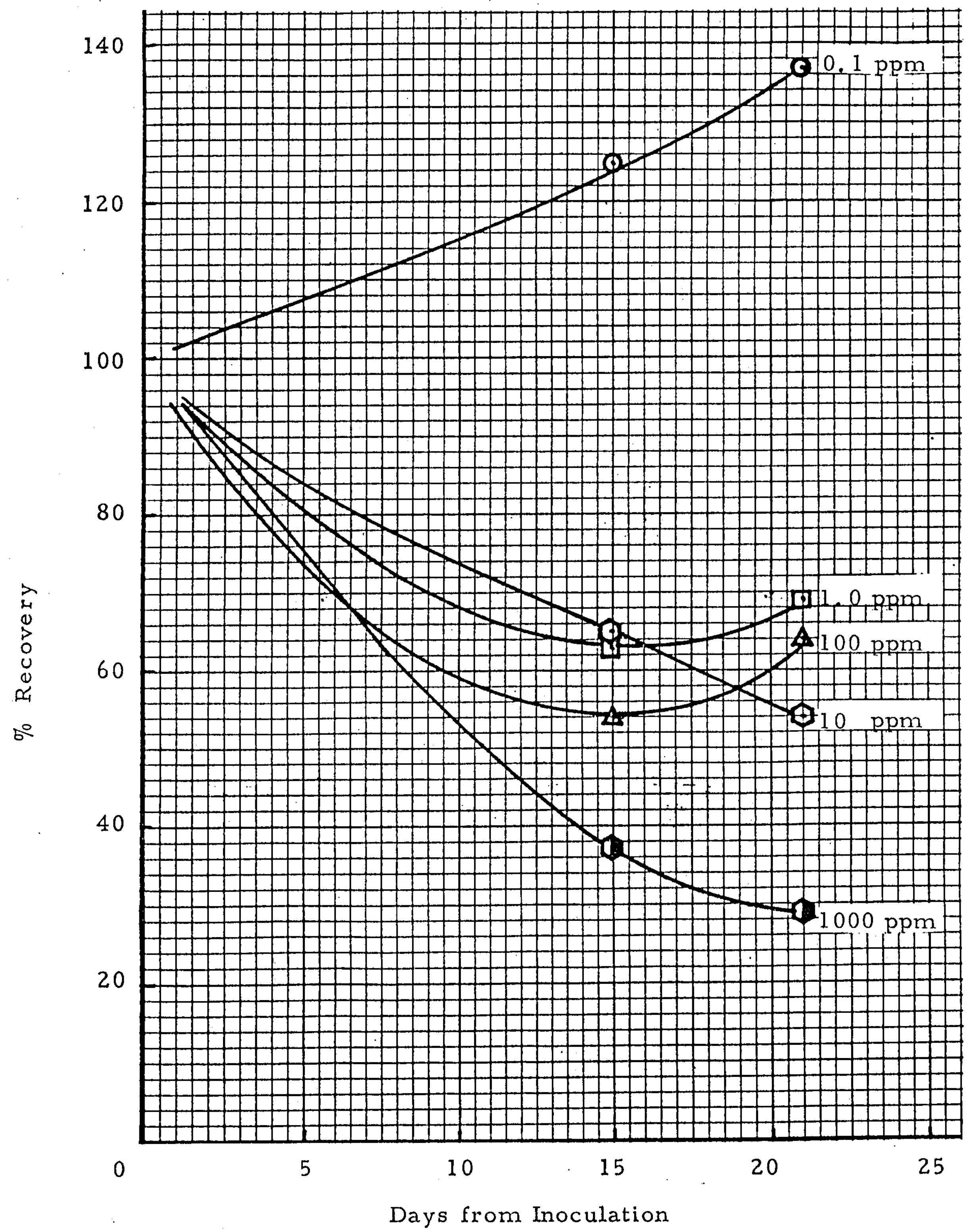
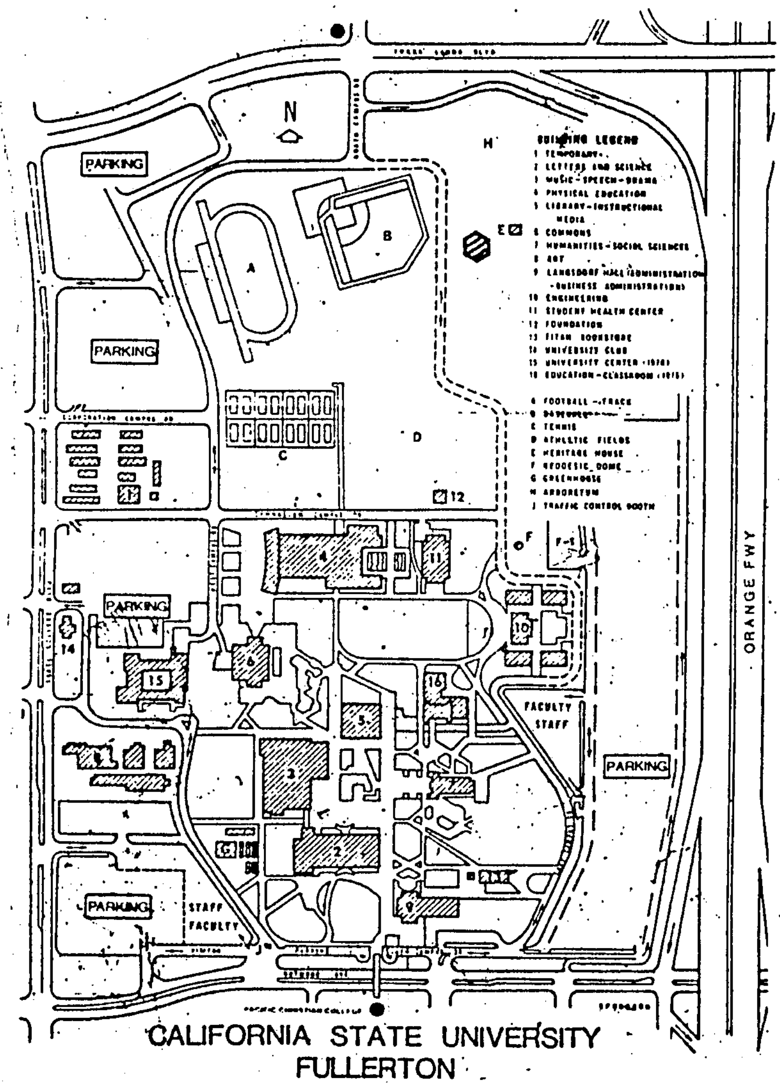


Figure 5. Recovery of DIMP from Intimately Mixed Soil Samples.



Sample Site

Figure 6. Location of Soil Sample from CSUF Campus.

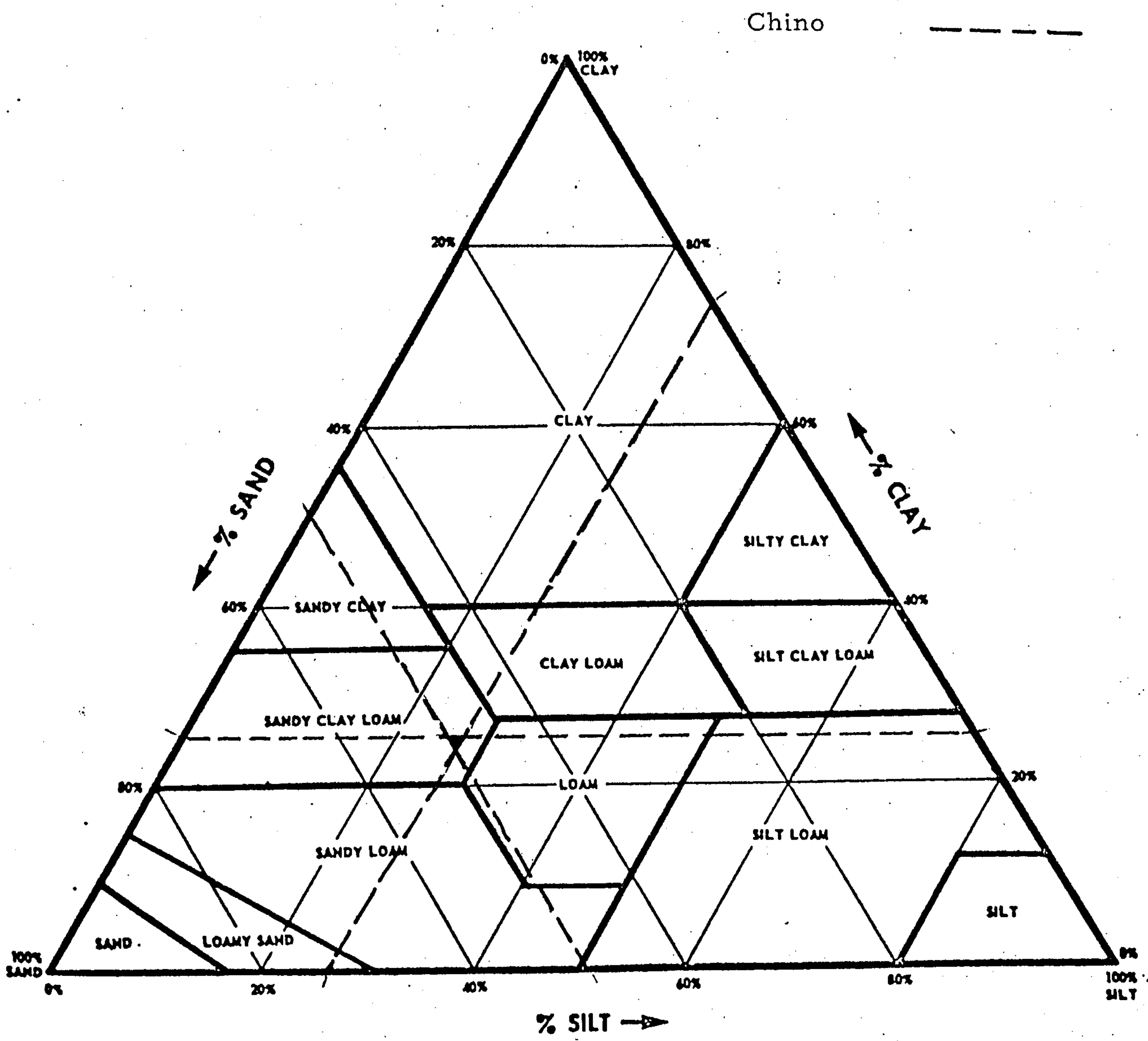


Figure 7. Textural Classification of Soils.

Figure 8. Site of Soil Procurement, Brawley, California.

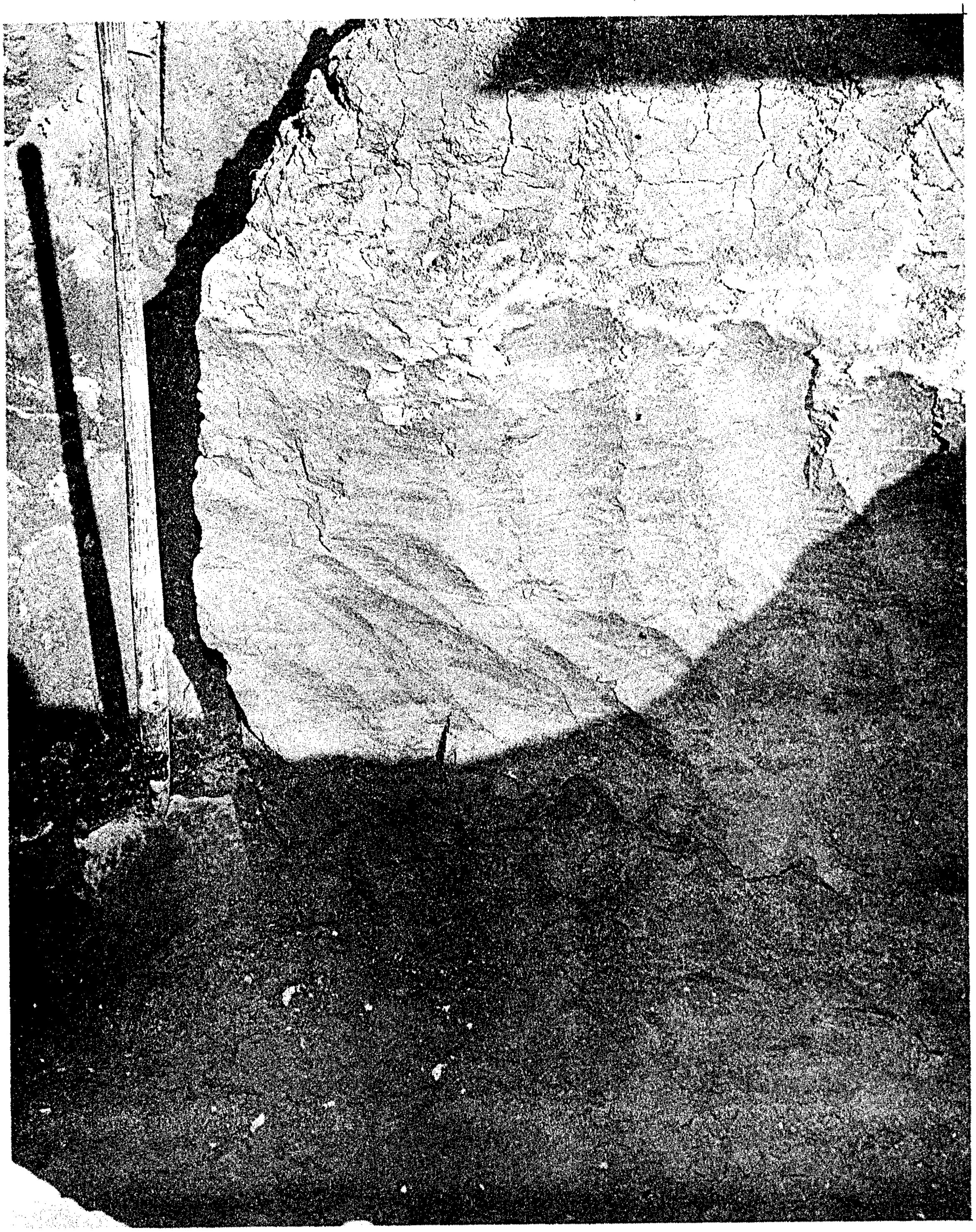


Figure 9. Sample Hole, Brawley, California.

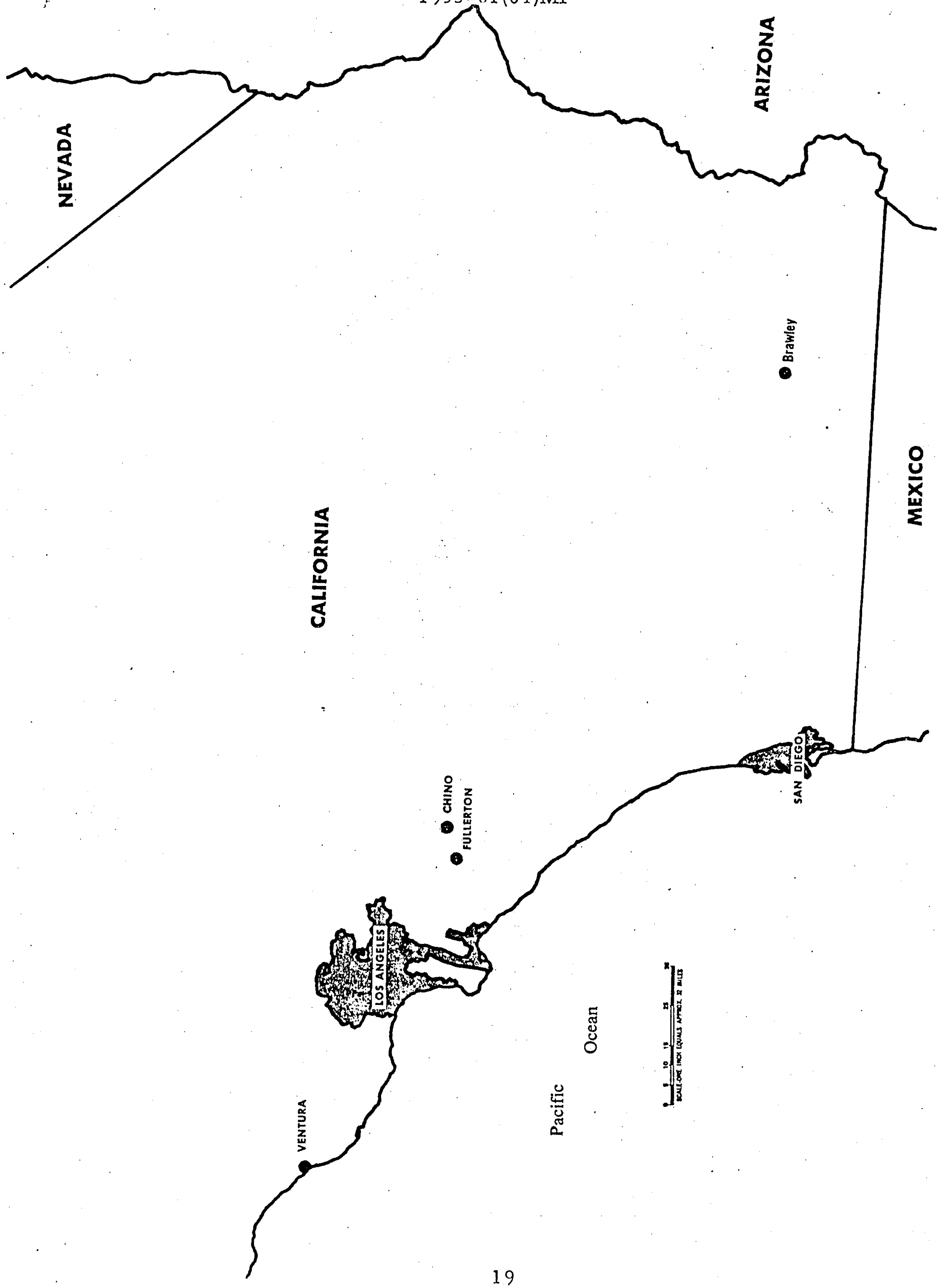


Figure 10. Geographical Location of AOMC Lysimeter Samples

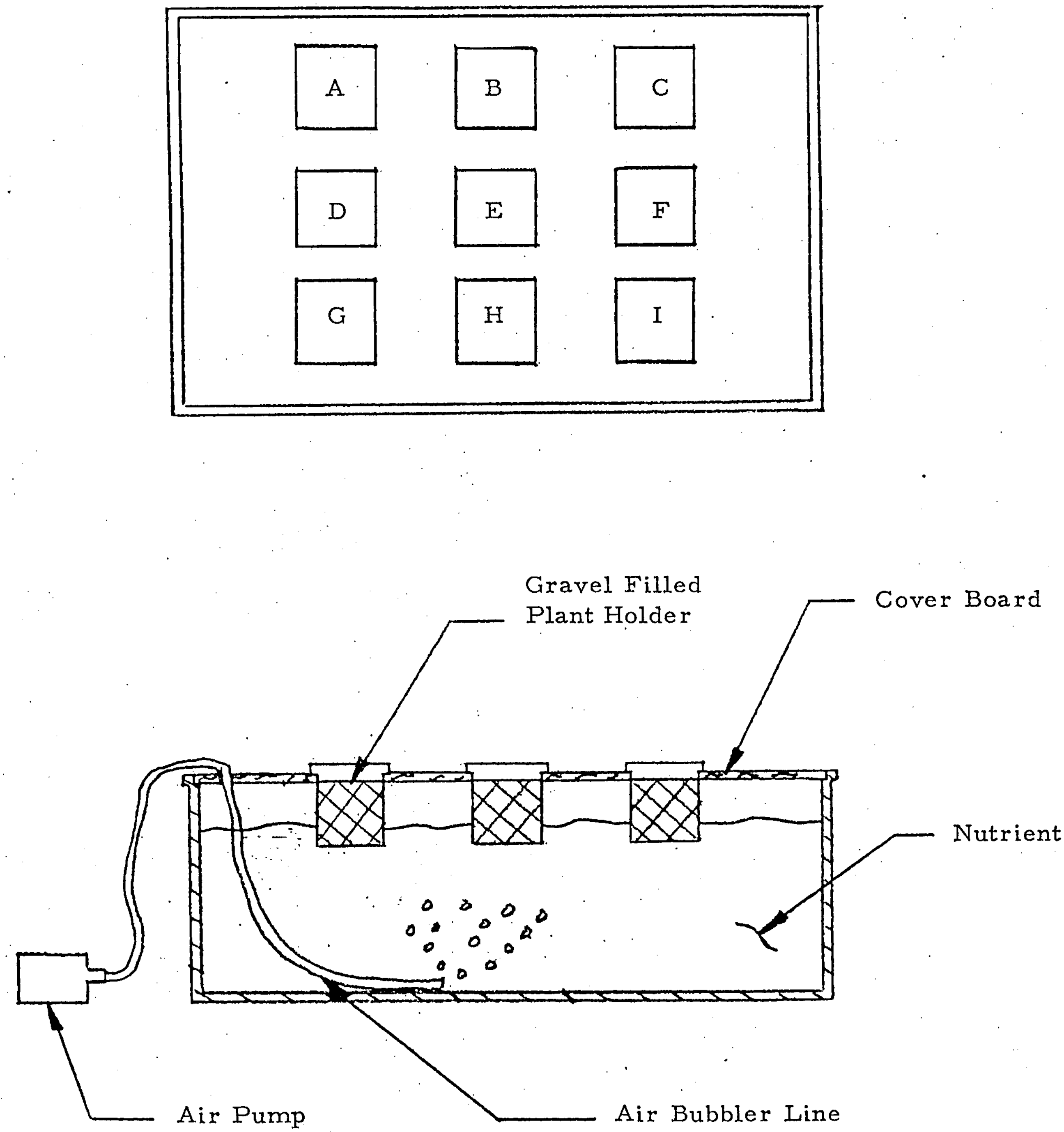


Figure 11. Set Up of Hydroponic Baths for Range Finding Experiments.

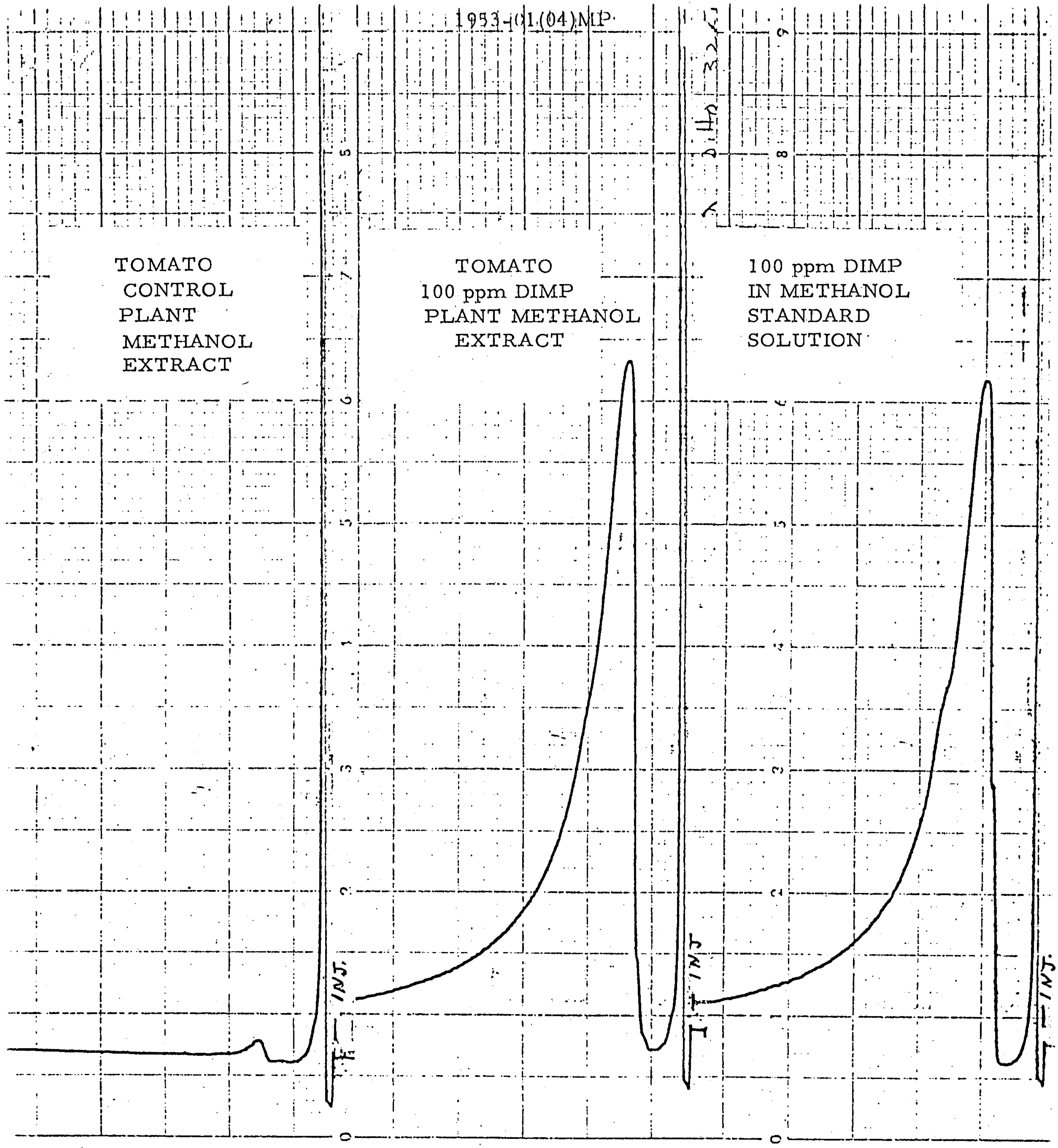


Figure 12. Chromatograms of Control and 100 ppm DIMP Tomato Plant Methanol Extracts and 100 ppm DIMP Standard in Methanol.